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A simple catalytic hydrolysis of chloropyrifos by Zr (IV), Hf (IV) and Cu (II) in aqueous acidic medium by HPLC

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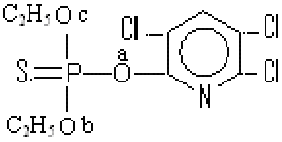
ABSTRACT

The effect of tetravalent and bivalent metal ions on the hydrolysis of Chloropyrifos O,O-diethyl (O-3,5,6-trichloropyrid-2-yl) phosphorothioate have been studied in acidic medium. The metal ions used as catalyst are Zr (IV), Hf (IV) and Cu (II). The rate maxima for the catalytic hydrolysis by Zr (IV) & Hf (IV) were observed around pH value 2,where as for cu (II) ions, it is observed at pH 6. The mechanism involves the coordination of metal ion to water molecule leads to the formation of octameric metal aqua complex. This complex remains in equilibrium with metal hydroxide ion (M-OH$^-$), nucleophiles (OH$^-$) are also available from these cations even in acidic aqueous solutions. Therefore an interaction of sulfur of P=S group with metal ion and an intramolecular nucleophilic attack of metal bound OH$^-$ at Phosphorus atom results in P-O bond cleavage to liberate the hydrolysis product 3,5,6- trichloro 2- pyridinol. The current study will help in investigating the catalytic behaviour of tetravalent and bivalent metals towards organophosphorus compounds in varied environment.

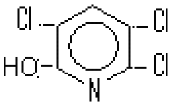
INTRODUCTION

Earlier reports include bivalent [1-3] and trivalent [4-7] metal catalyzed hydrolysis of organophosphorus esters and nucleotides like DNA and RNA. In recent years, much attention has been focused on the remarkable acceleration of phosphodiesters and nucleotide hydrolysis using tetravalent cations [8]. The cause of acceleration in rates has been attributed to the increase in water of hydration with increasing positive charge density on metal cation. However, tetravalent metal ion mediated hydrolysis of phosphorothionate esters has been reported in literature.

Chloropyrifos O,O-diethyl(O-3,5,6-trichloropyrid-2-yl)phosphorothioate, a phosphorothioate ester, was first introduced and patented by Dow Chemical Company in 1965[9] and is produced by the reaction of 3,5,6- trichloropyridin-2-ol (TCP) with O, O –diethyl phosphorochlorothioate.



Chloropyrifos
(thionate ester)
(a) L.G. 5.45[10]
(b, c) L.G. 15.5[11]



3,5,6- trichloro 2- pyridinol

Chloropyrifos, an important insecticide and accariside, is used to control many biting or sucking insect pests of agricultural crops [12]. It is highly toxic to mammals; the oral LD_{50} in rats being 2.9mg/kg. It has a half-life of 120 days in soil. It is hydrolyzed quickly in alkaline solution but persist under neutral and slightly acidic conditions [13].Chloropyrifos acts by the acetylcholinesterase causes an accumulation of acetylcholine (Ach), which is normally hydrolysed by the enzyme, paralyzing the synaptic site. The manifestations of organophosphate poisoning are associated with the increase in concentration of Ach at the neurone synapse [14]. Chloropyrifos is metabolized by fish and excreted in a changed from that is not an inhibitor of acetyl cholinesterase [15]. The uptake by plants is much faster than in fish [15]. This study includes hydrolysis Chloropyrifos by using Zr (IV) & Hf (IV) in, mild acidic aqueous solutions. A comparison has also been made with Cu (II), under similar condition.

MATERIALS AND METHODS

Experimental

The hydrolysis of Chloropyrifos in the presence of bivalent Cu (II) tetravalent Zr (IV) and Hf (IV) were examined. Commercial grade Chloropyrifos was obtained from India Pesticides Ltd. and were of (> 98% pure) technical grade and its degradation product was supplied by Aldrich (Sigma-Aldrich chemie, Germany). The metal salts, copper (II) chloride, Zirconium (IV) chloride, Hafnium (IV) chloride and HEPES buffer were also obtained from Aldrich. KCl was used AR grade and was obtained from central drug house (P) Ltd. Mumbai. The purity of the sample was checked by high performance liquid chromatographic analysis, and the characterization was by IR (Nujol): 3051, 2983, 1548, 1022, 835, 746cm^{-1} ^{1}H: 1.48 (t) (CH_2), 4.40(q)(CH_3), 7.9(aryl) & ^{31}P: 61.059; Mass M+ (m/z): 350.9, 314,197 (Base Peak),125,97,65,47.

HPLC analyses:

Chloropyrifos were analyzed using an LC-20AD (ULFA Prominence Liquid Chromatography (Shimadzu) equipped with a UV/Vis detector (at 280nm). A J'Sphere ODS-H80, C_{18}, 5µm, 250 mm X 4.6 mm i.d analytical column was used along with a phenomenex security guard column (4 mm X 2mm, C_{18}). Analyses were chromatographed with a pre-mixed mobile phase comprised of 50% Acetonitrile/ 45% water /5% 1mM acetic acid (pH4.30) at room temperature. The separate method was used to elute the analyte depending on the level of sensitivity [16].

Method: Injection of 20µl at a flow rate of 2ml/min for 10 min (5.0µg.mL^{-1}, 50 µg.mL^{-1}, and 500µg.mL^{-1}).

Retention time of the chloropyrifos is 5.6 min and its degradation product 3,5,6 trichloro-2 pyridinol is 2.0 min. A chromatogram of the 10.0µg.ml^{-1} working standard and 10.0µg.ml^{-1} 3,5,6 trichloro-2 pyridinol standard to demonstrate the separation of this compound is illustrate in fig-1.

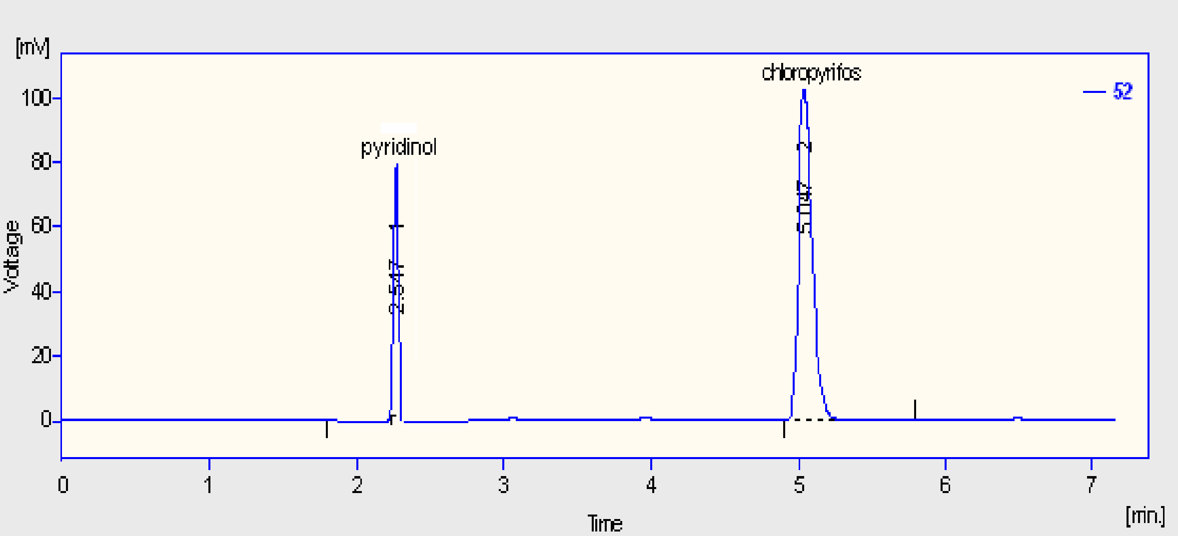


Figure – 1

Kinetic Measurement:
A typical kinetic run of [CPP]/[Zr^{4+}] (1:20) was prepared by dissolving KCl (.037g 1mM), $ZrCl_4$ (500 µg.ml^{-1}, 0.01M) in water in a 50 mL flask. The desired pH was then adjusted by using 0.1N HCl or 0.1N KOH. The solution at 6.0 pH was buffered by HEPES (0.122g, 1mM), prior to pH adjustment. All other runs performed at pH 1.0-5.0 were carried out in unbuffered aqueous solutions, because metal salt solutions themselves have sufficient buffer capacity [17].

The solution was chilled and to this, was added 1.25ml of stock solution of CPP in methanol (500 µg.ml^{-1}) and made up to the mark with chilled water. Equal volume of this was then properly Stoppard and placed simultaneously in a digital water bath maintained at 80 (±0.5)^{0}C. The test tubes were withdrawn one by one at definite time intervals and the liberated 3,5,6-trichloro2-pyridinol. Similarly, Kinetic runs with Varied [substrate]/[Metal] ratios e.g., 1:30, 1:15, 1:10, 1:5, 1:2 and 1:1 at different acidic regions, viz., at pH value 1.0-6.0 were performed.

RESULTS AND DISCUSSION

The results of the investigation of kinetics and hydrolysis of CPP catalyzed with Zr (IV) Hf (IV) & Cu (II) metal ion in acidic aqueous solution has been summarized in Table-1. These results clearly indicate the enhancement in reaction rate by decreasing pH of the medium. The rate increased remarkably with the addition of metal ions. All reaction were observed for more than three half lives and plots of log A_∞- A_0/ A_∞-A_t (where, $A_{0,}$ A_t and A_∞ are absorbance of 3,5,6-trichloro 2- pyridinol at time zero, t and infinity respectively) Versus time were linear indicating that ion catalysis are of first order with respect to the parent compound. Hydrolysis rate constant (k_{obs} in s^{-1}) correspond to the slope of these plots. Each run was performed in duplicate and found to be reproducible within ±5%. The kinetic rate data (Table 1) are the average value of rate constants obtained from duplicate runs. Considering that the [3,5,6- trichloro 2- pyridinol] obtained was equivalent to [CPP] lost and also by considering pKa values of leaving groups (LG)[18] a, b and c, the P-O bond fission, as shown in (I) seems to be probable reaction path way.

Table-1

pH	Zr4+	Hf4+	Cu2+
1	10.8	11.3	2.4
1.5	11.4	12.8	3.2
2	13.8	16.3	4.6
2.5	9.8	9.7	4.9
3	8.2	7.1	5.2
3.5	7.3	6.2	5.9
4	5.9	5.3	7.5
5	4.6	4.1	9.2
6	3.8	2.5	17.2
6.5	2.4	1.8	38.2
7	1.6	1.2	19.5

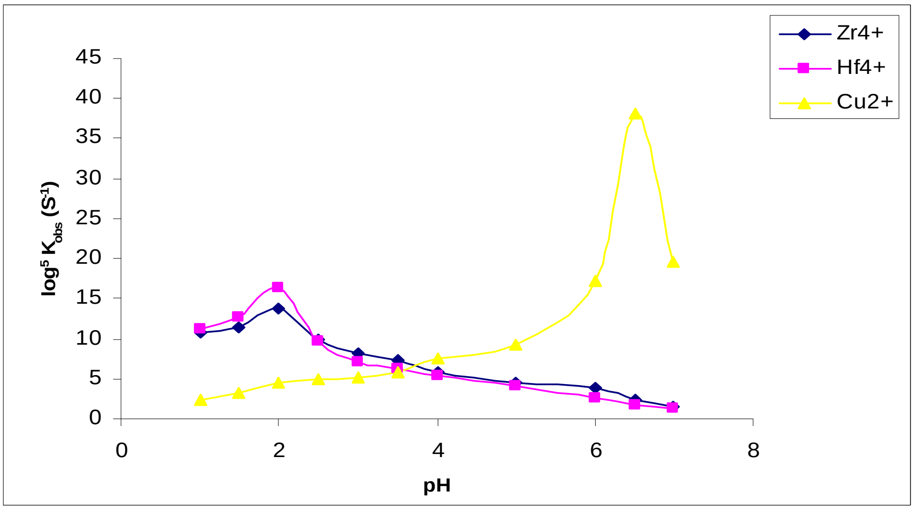
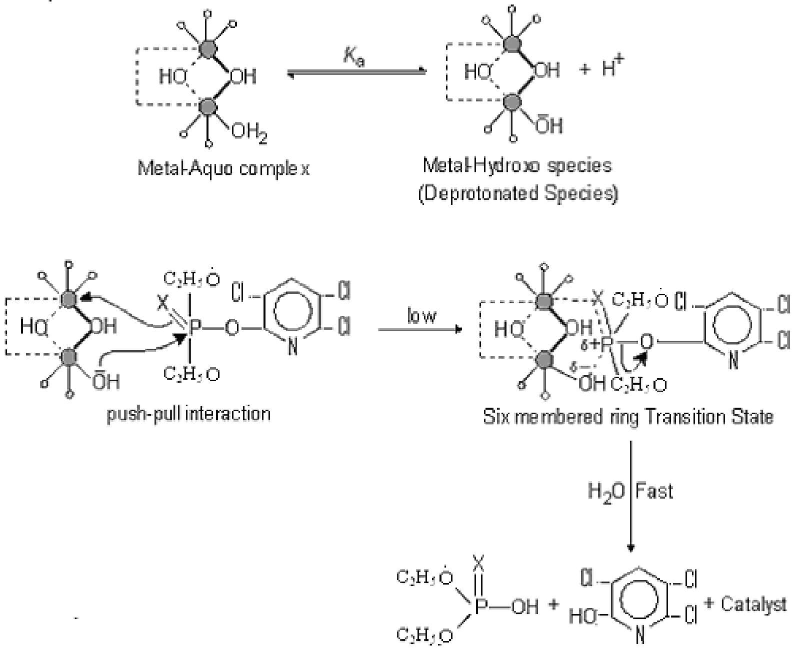


Fig-2: pH-rate constant profile for the tetravalent and bivalent metal catalyzed hydrolysis of Chloropyrifos at 80°C; [Substrate] =500µg.mL-1 and [Mn+] = 1500µg.mL-1

In our catalytic studies, we found that all metals require 20 fold excess concentrations over [CPP] for showing maximum catalysis in hydrolytic cleavages (Fig-2). The retardation in rate constant observed by adding more than 20 fold [metal] may be due to the alteration in shapes and sizes of the reactive M-OH$^-$ species produced by deprotonation of H_2O linked to metal ions. Relatively poor catalysis by Zr (IV) and Hf (IV) at pH 6.0 is probably due to the less solubility of their hydroxy species [19]. The fact that Cu (II) is a better catalyst ~ pH 6.0 may be due to the formation of readily soluble hydrated species of Cu^{2+} i.e. $[Cu(H_2O)_6]^{2+}$, which dissociated into reactive M^+-OH^- (i.e.$[Cu(H_2O)_5OH^-]^{2+}$) species[18]. The binding with sulphur of P=S group of CPP with metal ion, followed by an intramolecular attack of OH^- at phosphorus atom may be the reason of an enormous rate acceleration. Such push-pull mechanisms are frequently invoked to explain bivalent metal ion catalysis in the hydrolysis of phosphate esters [20-23]. Moreover, at around pH 2.0, Zr (IV) exists as coordination complex [24], $[Zr_8(OH)_{20}(H_2O)_{24}Cl_{12}]$, whose geometry has been determined to be octameric [24]. However, under similar condition Hf (IV) exhibited a similar chemistry [19]. Bridging of two tetramers via four single OH^- bridges forms these octameric species and each metal cations of the octamer is bound to three H_2O molecules. Since lewis acidity and acidity of metal cation, highly charged cation, such as Zr^{4+}, Hf^{4+},Ce^{4+} are particularly reactive towards bis(p-nitrophenyl) phosphate. The metal-bound water molecule (i.e., $M\text{-}OH_2$) on deprotonation gives rise to $M\text{-}OH^-$ anion and exists in equilibrium with each other. The reported pKa of metal-bound water molecule is ≤ 0.6 for Zr (IV) and ≤ 1.1 for Hf (IV), and M-OH nucleophiles would be available from these cations even in acidic aqueous solutions [25]. Typically, one zirconium atom of the octameric metal-complex seems to be involved in metal-ester bonding while the adjacent metal bound OH^- gives six membered ring type transition state[24-26] Via intramolecular nucleophilic attack at phosphorus atom, which subsequently breaks into 3,5,6- trichloro 2- pyridinol, diethyl phosphorothioic acid and the catalyst as shown by scheme 1. (The scheme shows only the connectivity of two metal cations; rest of the octamer has been represented by the dotted line).



The dotted line (⬚) represents the octameric or dimeric structure of the metal aquo-complex, the symbols o and ● stands for H_2O and metal cations involved in the complex formation

CONCLUSION

$Zr4^+$ at pH 2.0 and Cu^{2+} at pH 6.0 are more reactive towards the hydrolysis of Chloropyrifos, a Model Phosphorothionate ester. The current study will help in investigating the hydrolytic behavior of bivalent and tetravalent metals towards organophosphorus compounds in varied environment. Our study will contribute in the formulation of a decontaminant for organophosphorus compounds of biological significance.

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